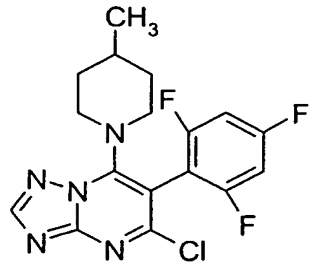
Fungicidal mixtures for controlling rice pathogens

Description

The present invention relates to fungicidal mixtures for controlling rice pathogens, which mixtures comprise, as active components,

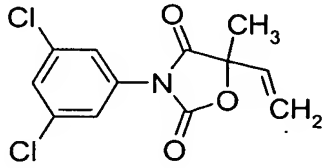
1) the triazolopyrimidine derivative of the formula I



I

and

2) vinclozolin of the formula II



II

in a synergistically effective amount.

Moreover, the invention relates to a method for controlling harmful fungi using mixtures of the compound I with the compound II and to the use of the compound I with the compound II for preparing such mixtures and compositions comprising these mixtures.

The compound I, 5-chloro-7-(4-methylpiperidin-1-yl)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine, its preparation and its action against harmful fungi are known from the literature (WO 98/46607).

The compound II, 3-(3,5-dichlorophenyl)-5-methyl-5-vinyloxazolidine-2,4-dione, its preparation and its action against harmful fungi are likewise known from the literature (DE-A 22 07 576; common name vinclozolin).

Mixtures of triazolopyrimidins with vinclozolin are known in a general manner from EP-A 988 790. The compound I is embraced by the general disclosure of this publication,

but not explicitly mentioned. Accordingly, the combination of compound I with vinclozolin is novel.

The synergistic mixtures known from EP-A 988 790 are described as being fungicidally active against various diseases of cereals, fruit and vegetables, for example mildew on wheat and barley or gray mold on apples.

It is an object of the present invention to provide, with a view to effective control of rice pathogens at application rates which are as low as possible, mixtures which, at a reduced total amount of active compounds applied, have an improved effect against the rice pathogens.

Owing to the special cultivation conditions of rice plants, the requirements that a rice fungicide has to meet are considerably different from those that fungicides used in cereal or fruit growing have to meet. There are significant differences in the application method: in rice crops, the fungicide is typically applied directly onto the soil during or shortly after sowing. The fungicide is taken up into the plant via the roots and transported in the sap of the plant to the plant parts to be protected. In contrast, in cereal or fruit growing, the fungicide is usually applied onto the leaves or the fruits; accordingly, in these crops the systemic action of the active compounds is considerably less important.

Moreover, rice pathogens are typically different from those in cereals or fruit. *Pyricularia oryzae* and *Corticium solani* (syn. *Rhizoctonia sasakii*) are the pathogens of the diseases most prevalent in rice plants. *Rhizoctonia sasakii* is the only pathogen of agricultural significance from the sub-class *Agaricomycetidae.* In contrast to most other fungi, this fungus attacks the plant not via spores but via a mycelium infection.

For this reason, findings concerning the fungicidal activity in the cultivation of cereals or fruit cannot be transferred to rice crops.

It is an object of the present invention to provide, with a view to effective control of rice pathogens at application rates which are as low as possible, mixtures which, at a reduced total amount of active compounds applied, have an improved effect against the harmful fungi.

We have found that this object is achieved by the mixtures defined at the outset. Surprisingly, we have found that the vinclozolin mixtures defined at the outset allow considerably better control of rice pathogens than the vinclozolin mixtures of the triazolopyrimidine compounds known from EP-A 988 790. Moreover, we have found that

simultaneous, that is joint or separate, application of the compound I and the compound II or successive application of the compound I and the compound II allows better control of rice pathogens than is possible with the individual compounds.

When preparing the mixtures, it is preferred to employ the pure active compounds I and II, to which further active compounds against harmful fungi or other pests, such as insects, arachnids or nematodes, or else herbicidal or growth-regulating active compounds or fertilizers can be added as required.

Other suitable active compounds in the above sense are in particular active compounds selected from the following groups:

- acylalanines, such as benalaxyl, metalaxyl, ofurace, oxadixyl,
- aminderivate, such as aldimorph, dodemorph, fenpropimorph, fenpropidin, guazatine, iminoctadine, tridemorph,
- anilinopyrimidines, such as pyrimethanil, mepanipyrim or cyprodinil,
- antibiotics, such as cycloheximid, griseofulvin, kasugamycin, natamycin, polyoxin or streptomycin,
- azoles, such as bitertanol, bromoconazole, cyproconazole, difenoconazole, dinitroconazole, enilconazole, epoxiconazole, fenbuconazole, fluquiconazole, flusilazole, flutriafol, hexaconazole, imazalil, ipconazole, metconazole, myclobutanil, penconazole, propiconazole, prochloraz, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triflumizol, triticonazole,
- dicarboximides, such as myclozolin,
- dithiocarbamates, such as ferbam, nabam, mancozeb, metam, propineb, polycarbamat, ziram, zineb,
- heterocyclic compounds, such as anilazin, benomyl, boscalid, carbendazim, carboxin, oxycarboxin, cyazofamid, dazomet, dithianon, famoxadon, fenamidon, fuberidazole, flutolanil, furametpyr, isoprothiolan, mepronil, nuarimol, penthiopyrad, probenazole, pyroquilon, quinoxyfen, silthiofam, thiabendazol, thifluzamid, tiadinil, tricyclazole, triforine,
- nitrophenyl derivatives, such as binapacryl, dinocap, dinobuton, nitrophthal-isopropyl,
- phenylpyrroles, such as fenpiclonil or fludioxonil,
- sulfur or copper,
- other fungicides, such as acibenzolar-S-methyl, fungicides carpropamid, chlorothalonil, cyflufenamid, cymoxanil, benthiavalicarb, diclomezin, diclocymet, diethofencarb, edifenphos, ethaboxam, fenhexamid, fentin-acetate, fenoxanil, ferimzone, fluazinam, fosetyl, fosetyl-aluminum, phosphorous acid iprovalicarb, hexachloroben-

- zene, metrafenon, pencycuron, propamocarb, phthalid, toloclofos-methyl, quintozene, zoxamid,
- strobilurins, such as azoxystrobin, dimoxystrobin, enestroburin, fluoxastrobin, kresoxim-methyl, metominostrobin, orysastrobin, pyraclostrobin or trifloxystrobin,
- sulfenic acid derivatives, such as captafol, captan, dichlofluanid,
- cinnamides and analogous compounds, such as dimethomorph, flumetover or flumorph.

In one embodiment of the mixtures according to the invention, a further fungicide III or two fungicides III and IV are added to the compounds I and II.

From among these, suitable components III and, if appropriate, IV are in particular the anilinopyrimidines and heterocyclic compounds.

Preference is given to mixtures of the compounds I and II with a component III.

Particular preference is given to mixtures of the compounds I and II.

The mixtures of the compounds I and II or the simultaneous (joint or separate) use of the compound I and the compound II are distinguished by an outstanding effectiveness against rice pathogens from the class of the *Ascomycetes*, *Deuteromycetes* and *Basidiomycetes*. They have high systemic activity and can therefore be employed for seed dressing, and also as foliar and soil fungicides.

They are of particular importance for the control of harmful fungi on rice plants and seeds thereof, such as *Bipolaris* and *Drechslera* species, and also *Pyricularia oryzae*. They are particularly suitable for controlling rice blast caused by *Pyricularia oryzae*.

In addition, the combination according to the invention of the compounds I and II is also suitable for controlling other pathogens, such as, for example, *Septoria* and *Puccinia* species in cereals and *Alternaria* and *Boytritis* species in vegetables, fruit and grapevines.

The compound I and the compound II can be applied simultaneously, that is jointly or separately, or in succession, the sequence, in the case of separate application, generally not having any effect on the result of the control measures.

The compound I and the compound II are usually applied in a weight ratio of from 100:1 to 1:100, preferably from 20:1 to 1:20, in particular from 10:1 to 1:10.

The components III and, if appropriate, IV are, if desired, added in a ratio of 20:1 to 1:20 to the compound I.

Depending on the type of the compound and of the desired effect, the application rates of the mixtures according to the invention are from 5 g/ha to 2000 g/ha, preferably from 50 to 1500 g/ha, in particular from 50 to 1000 g/ha.

Correspondingly, the application rates for the compound I are generally from 1 to 1000 g/ha, preferably from 10 to 900 g/ha, in particular from 20 to 750 g/ha.

Correspondingly, the application rates for compound II are generally from 1 to 1500 g/ha, preferably from 10 to 1000 g/ha, in particular from 20 to 750 g/ha.

In the treatment of seed, application rates of mixture of generally from 1 to 1000 g/100 kg of seed, preferably from 1 to 200 g/100 kg, in particular from 5 to 100 g/100 kg, are used.

In the control of harmful fungi phytopathogenic to rice plants, the separate or joint application of the compounds I and II or of the mixtures of the compounds I and II is carried out by spraying or dusting the seeds, the seedlings, the plants or the soil before or after sowing of the plants or before or after emergence of the plants. Joint or separate application of the compounds can also be carried out by applying granules or by dusting the soil. In another preferred embodiment of the method the application of the compounds is carried out by spraying the leaves.

The mixtures according to the invention, or the compounds I and II, can be converted into the customary formulations, for example solutions, emulsions, suspensions, dusts, powders, pastes and granules. The use form depends on the particular intended purpose; in each case, it should ensure a fine and even distribution of the compound according to the invention.

The formulations are prepared in a known manner, for example by extending the active compound with solvents and/or carriers, if desired using emulsifiers and dispersants. Solvents/auxiliaries suitable for this purpose are essentially:

- water, aromatic solvents (for example Solvesso products, xylene), paraffins (for example mineral oil fractions), alcohols (for example methanol, butanol, pentanol, benzyl alcohol), ketones (for example cyclohexanone, gamma-butyrolactone), pyrrolidones (NMP, NOP), acetates (glycol diacetate), glycols, fatty acid dimethylamides, fatty acids and fatty acid esters. In principle, solvent mixtures may also be used,

- carriers, such as ground natural minerals (for example kaolins, clays, talc, chalk) and ground synthetic minerals (for example highly disperse silica, silicates); emulsifiers, such as nonionogenic and anionic emulsifiers (for example polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates), and dispersants, such as lignosulfite waste liquors and methylcellulose.

Suitable surfactants are alkali metal, alkaline earth metal and ammonium salts of lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid, dibutylnaphthalenesulfonic acid, alkylarylsulfonates, alkyl sulfates, alkylsulfonates, fatty alcohol sulfates, fatty acids and sulfated fatty alcohol glycol ethers, furthermore condensates of sulfonated naphthalene and naphthalene derivatives with formaldehyde, condensates of naphthalene or of naphthalenesulfonic acid with phenol and formaldehyde, polyoxyethylene octylphenyl ether, ethoxylated isooctylphenol, octylphenol and nonylphenol, alkylphenyl polyglycol ethers, tributylphenyl polyglycol ethers, tristearylphenyl polyglycol ethers, alkylaryl polyether alcohols, alcohol and fatty alcohol ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol polyglycol ether acetals, sorbitol esters, lignosulfite waste liquors and methylcellulose.

Substances which are suitable for the preparation of directly sprayable solutions, emulsions, pastes or oil dispersions are mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons, for example toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or their derivatives, methanol, ethanol, propanol, butanol, cyclohexanol, cyclohexanone, isophorone, highly polar solvents, for example dimethyl sulfoxide, N-methylpyrrolidone or water.

Powders, materials for spreading and dustable products can be prepared by mixing or concomitantly grinding the active substances with a solid carrier.

Granules, for example coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active compounds to solid carriers. Examples of solid carriers are mineral earths, such as silica gels, silicates, talc, kaolin, attaclay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, such as, for example, ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders and other solid carriers.

In general, the formulations comprise from 0.01 to 95% by weight, preferably from 0.1 to 90% by weight, of the active compounds. The active compounds are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to the NMR spectrum).

The following are examples of formulations: 1. Products for dilution with water

A) Water-soluble concentrates (SL)

10 parts by weight of the active compounds are dissolved in water or in a water-soluble solvent. As an alternative, wetters or other auxiliaries are added. The active compound dissolves upon dilution with water.

B) Dispersible concentrates (DC)

20 parts by weight of the active compounds are dissolved in cyclohexanone with addition of a dispersant, for example polyvinylpyrrolidone. Dilution with water gives a dispersion.

C) Emulsifiable concentrates (EC)

15 parts by weight of the active compounds are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5% strength). Dilution with water gives an emulsion.

D) Emulsions (EW, EO)

40 parts by weight of the active compounds are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5% strength). This mixture is introduced into water by means of an emulsifying machine (Ultraturrax) and made into a homogeneous emulsion. Dilution with water gives an emulsion.

E) Suspensions (SC, OD)

In an agitated ball mill, 20 parts by weight of the active compounds are comminuted with addition of dispersants, wetters and water or an organic solvent to give a fine active compound suspension. Dilution with water gives a stable suspension of the active compound.

F) Water-dispersible granules and water-soluble granules (WG, SG)

50 parts by weight of the active compounds are ground finely with addition of dispersants and wetters and prepared as water-dispersible or water-soluble granules by means of technical appliances (for example extrusion, spray tower, fluidized bed). Dilution with water gives a stable dispersion or solution of the active compound.

G) Water-dispersible powders and water-soluble powders (WP, SP)

75 parts by weight of the active compounds are ground in a rotor-stator mill with addition of dispersants, wetters and silica gel. Dilution with water gives a stable dispersion or solution of the active compound.

2. Products to be applied undiluted

H) Dustable powders (DP)

5 parts by weight of the active compounds are ground finely and mixed intimately with 95% of finely divided kaolin. This gives a dustable product.

I) Granules (GR, FG, GG, MG)

0.5 part by weight of the active compounds is ground finely and combined with 95.5% of carriers. Current methods are extrusion, spray-drying or the fluidized bed. This gives granules to be applied undiluted.

J) ULV solutions (UL)

10 parts by weight of the active compounds are dissolved in an organic solvent, for example xylene. This gives a product to be applied undiluted.

The active compounds can be used as such, in the form of their formulations or the use forms prepared therefrom, for example in the form of directly sprayable solutions, powders, suspensions or dispersions, emulsions, oil dispersions, pastes, dustable products, materials for spreading, or granules, by means of spraying, atomizing, dusting, spreading or pouring. The use forms depend entirely on the intended purposes; they are intended to ensure in each case the finest possible distribution of the active compounds according to the invention.

Aqueous use forms can be prepared from emulsion concentrates, pastes or wettable powders (sprayable powders, oil dispersions) by adding water. To prepare emulsions, pastes or oil dispersions, the substances, as such or dissolved in an oil or solvent, can be homogenized in water by means of a wetter, tackifier, dispersant or emulsifier. However, it is also possible to prepare concentrates composed of active substance, wetter, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil, and such concentrates are suitable for dilution with water.

The active compound concentrations in the ready-to-use preparations can be varied within relatively wide ranges. In general, they are from 0.0001 to 10%, preferably from 0.01 to 1%.

The active compounds may also be used successfully in the ultra-low-volume process (ULV), it being possible to apply formulations comprising over 95% by weight of active compound, or even to apply the active compound without additives.

Oils of various types, wetters, adjuvants, herbicides, fungicides, other pesticides, or bactericides may be added to the active compounds, even, if appropriate, not until immediately prior to use (tank mix). These agents can be admixed with the compositions according to the invention typically in a weight ratio of from 1:10 to 10:1.

The compounds I and II or the mixtures or the corresponding formulations are applied by treating the harmful fungi or the plants, seeds, soils, areas, materials or spaces to be kept free therefrom with a fungicidally effective amount of the mixture or, in the case of separate application, of the compounds I and II. Application can be carried out before or after infection by the harmful fungi.

The fungicidal action of the compound and of the mixtures may be revealed by the following tests:

The active compounds, separately or jointly, were prepared as a stock solution comprising 0.25% by weight of active compound in acetone or DMSO. 1% by weight of the emulsifier Uniperol® EL (wetting agent having emulsifying and dispersing action based on ethoxylated alkylphenols) was added to this solution, and the mixture was appropriately diluted with water to the desired concentration.

Use example – protective activity against rice blast caused by *Pyricularia oryzae*

Leaves of potted rice seedlings of the cultivar "Tai-Nong 67" were sprayed to runoff point with an aqueous suspension of the concentration of active compound stated below. The next day, the plants were inoculated with an aqueous spore suspension of *Pyricularia oryzae*. The test plants were then placed in climatized chambers at 22-24°C and 95-99% relative atmospheric humidity for 6 days. The extent of the development of the infection on the leaves was then determined visually.

Evaluation is carried out by determining the percentage of infected leaf area. These percentages were converted into efficacies.

The efficacy (E) is calculated as follows using Abbot's formula:

$$E = (1 - \alpha/\beta) \cdot 100$$

α corresponds to the fungicidal infection of the treated plants in % and

β corresponds to the fungicidal infection of the untreated (control) plants in %

An efficacy of 0 means that the infection level of the treated plants corresponds to that of the untreated control plants; an efficacy of 100 means that the treated plants are not infected.

The expected efficacies of mixtures of active compounds are determined using Colby's formula (Colby, R.S. Weeds, 15, 20-22, 1967) and compared with the observed efficacies.

Colby's formula:

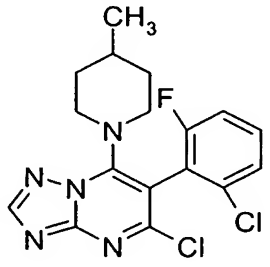
$$E = x + y - x \cdot y/100$$

E expected efficacy, expressed in % of the untreated control, when using the mixture of the active compounds A and B at the concentrations a and b

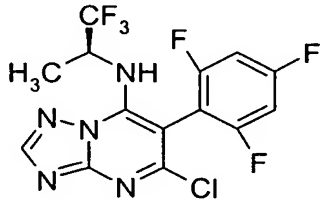
x efficacy, expressed in % of the untreated control, when using the active compound A at the concentration a

y efficacy, expressed in % of the untreated control, when using the active compound B at the concentration b

The comparative compounds used were the compounds A and B known from the vinclozolin mixtures described in EP-A 988 790:



A



B

Table A – Individual active compounds

Example	Active compound	Concentration of active compound in the spray liquor [ppm]	Efficacy in % of the untreated control
1	control (untreated)	-	(69 % infection)
2	I	4 1	28 13
3	II (vinclozolin)	4 1	0 0
4	comparative compound A	4 1	13 0
5	comparative compound B	4 1	57 13

Table B – Mixtures according to the invention

Example	Mixture of active compounds Concentration Mixing ratio	Observed efficacy	Calculated efficacy*)
6	I + II 4 + 1 ppm 4:1	78	28
7	I + II 4 + 4 ppm 1:1	57	13
8	I + IIa 1 + 4 ppm 1:4	71	13

*) calculated efficacy using Colby's formula

Table C – comparative experiments

vinclozolin mixtures known from EP-A 988 780

Example	Mixture of active compounds Concentration Mixing ratio	Observed efficacy	Calculated efficacy*)
9	A + II 4 + 1 ppm 4:1	28	13
10	A + II 1 + 1 ppm 1:1	0	0
11	A + II 1 + 4 ppm 1:4	0	0
12	B + II 4 + 1 ppm 4:1	42	57
13	B + II 1 + 1 ppm 1:1	28	13
14	B + II 1 + 4 ppm 1:4	42	13

*) calculated efficacy using Colby's formula

The test results show that, by virtue of strong synergism, the mixtures according to the invention are considerably more effective against rice blast than the vinclozolin mixtures, known from EP-A 988 780, of the comparative compounds.